

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE In re Patent Application of:

Inventor:

OKA, et al

Group Art Unit:

1752

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Examiner:

Thorl Chea

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Title:

PHOTOTHERMOGRAPHIC MATERIAL

DECLARATION UNDER 37 C.F.R. \$1.132

Commissioner for Patents

(P.O. Box 1450

Alexandria, VA 22313-1450)

Sir:

I, Seiichi Yamamoto, do declare and state as follows:

I graduated from Tohoku University with a Master's Degree in Chemistry in March 1990;

I joined Fuji Photo Film Co., Ltd. in April 1990, and since that time I have been engaged in research and development in the field of silver halide photosensitive materials for printing, and since March 2000, in the field

of silver halide photosensitive materials for medical use at Ashigara Laboratory;

I am a co-inventor of the subject matter disclosed and claimed in the above-identified application; and

I am familiar with the Office Action of November 23, 2005, and understand that the Examiner has rejected Claims 1-9 under 35 U.S.C. § 103(a) as being unpatentable over the combination of Okada et al (US Patent No. 5,952,167), Ikari (US Patent No. 6,482,583), Siga et al (US Patent No. 4,332,889) and Toya et al (US Patent No. 5,998,126) and Claims 10, 13-20 under 35 U.S.C. § 103(a) as being unpatentable over Ito (US Patent No. 6,376,167).

The following additional comparative experiments were carried out by me or under my supervision in order to make the advantages of the subject matter clearer.

Experiment I

Samples 3d, 3e, 5d, 5e, 6d, 6e, 7d, 7e, 8d, 8e, 9d and 9e were prepared and added to the Experiment B in the declaration dated on January 19, 2005.

Samples 3d, 3e, 5d, 5e, 6d, 6e, 7d, 7e, 8d, 8e, 9d and 9e were prepared in the same manner as in Example 4 described in Applicants' Specification, except that the doped metals

in the photosensitive halide emulsion and their amount were changed to those as shown in Table I below, so that the amount of metal used singly becomes equal to the combination of the pair.

Grains in the silver halide used in Example 4 were pure silver iodide as described in Applicants' Specification, on page 161 lines 2-6.

Samples 3d, 3e, 5d, 5e, 6d, 6e, 7d, 7e, 8d, 8e, 9d and 9e were processed and evaluated in the same manner as in Example 4 described in Applicants' Specification.

The results obtained are listed in following currently amended Table I.

TABLE I

Sample	First	First	Second	Second	Dmin	Sensit	Printout	Remarks
No.	Metal	Metal	Metal	Metal		ivity	performa	
		Amount		Amount	1		nde	
		mol/Ag		mol/Ag				
3a	Ir	5×10 ⁻⁴	~	-	0.17	100	0.11	Comparative
		~~~						Example
<b>3</b> b	-	-	Fe	3×10 ⁻³	0.17	103	0.10	Comparative
								Example
3d	_	-	Fe	5×10 ⁻⁴	0.17	102	0.10	Comparative

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	<del></del> r					<del></del>	γ	
	_							Example
3е	Ir	2.5	Fe	2.5	0.16	106	0.07	Present
		×10 ⁻⁴		×10 ⁻⁴				Invention
3′	Ir	5×10 ⁻¹	Fe	3×10 ⁻³	0.16	107	0.07	Present
								Invention
10-1	Ir	5×10 ⁻¹	Au	3×10 ⁻³	0.18	110	0.12	Comparative
								Example
5a	Cu	5×10 ⁻⁴	-	-	0.17	101	0.10	Comparative
								Example
5b	-	-	Fe	3×10 ⁻³	0.17	103	0.10	Comparative
								Example
5d	-	-	Fe	5×10 ⁻⁴	0.17	102	0.10	Comparative
								Example
5e	Cu	2.5	Fe	2.5	0.16	104	0.07	Present
	-	×10 ⁻¹		×10 ⁻⁴				Invention
5*	Cu	5×10⁻⁴	Fe	3×10 ⁻³	0.16	105	0.07	Present
								Invention
10-2	Cu	5×10 ⁻⁴	Au	3×10 ⁻³	0.18	109	0.11	Comparative
								Example
ба	Fe	5×10 ⁻⁴	_	-	0.17	101	0.10	Comparative
								Example
6b	_	-	Pt	3×10 ⁻³	0.17	102	0.10	Comparative
								Example
6d	_	_	Pt	5×10⁻⁴	0.17	101	0.10	Comparative
								Example

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бе	Fe	2.5	Pt	2.5	0.16	106	0.08	Present
		×10 ⁻¹		×10 ⁻⁴				Invention
6'	Fe	5×10 ⁻⁴	Pt	3×10 ⁻³	0.16	106	0.08	Present
	_							Invention
7a	Os	5×10 ⁻⁴	-	-	0.17	100	0.10	Comparative
								Example
7b	-	_	Fe	3×10 ⁻³	0.17	103	0.10	Comparative
	_							Example
7d	-	\ - · · · ·	Fe	5×10 ⁻⁴	0.17	102	0.10	Comparative
								Example
7e	Os	2.5	Fe	2.5	0.16	105	0.07	Present
-		×10 ⁻¹		×10 ⁻⁴				Invention
7′	Os	5×10 ⁻⁴	Fe	3×10 ⁻³	0.16	106	0.07	Present
	<u> </u>		<u> </u>		<u></u>			Invention
10-3	Os	5×10 ⁻⁴	Au	3×10 ⁻³	0.18	110	0.11	Present
								Invention
9a	Ru	5×10⁻⁴	-	-	0.17	104	0.11	Comparative
	<u>'</u>							Example
3b	-	-	Fe	3×10 ⁻³	0.17	103	0.10	Comparative
		ļ						Example
3d	_	-	Fe	5×10 ⁻⁴	0.17	101	0.10	Comparative
								Example
e	Ru	2.5	Fe	2.5	0.16	105	0.07	Present
		×10 ⁻⁴	· · · · · · · · · · · · · · · · · · ·	×10 ⁻⁴				Invention
c	Ru	5×10 ⁻⁴	Fe	3×10 ⁻³	0.17	106	0.07	Present

		-y-						
								Invention
9a	-	-	-	-	0.18	98	0.12	Comparative
								Example
9ъ	-	-	Cu	3×10 ⁻³	0.17	101	0.11	Comparative
								Example
9d	-	_	Cu	5×10 ⁻⁴	0.17	100	0.11	Comparative
								Example
9e	Ru	2.5	Cu	2.5	0.16	103	0.06	Present
		×10 ⁻⁴		×10 ⁻⁴				Invention
9c	Ru	5×10 ⁻⁴	Cu	3×10 ⁻³	0.05	104	0.06	Present
	ļ							Invention
10-4	_	_	Aυ	3×10 ⁻³	0.19	109	0.12	Comparative
								Example
10-5	Fe	5×10 ⁻⁴	Au	3×10 ⁻³	0.19	109	0.11	Comparative
								Example

Note: For "Au", Potassium chloroaurate, which is typical as an Au-sensitizer, was used, and substituted at an amount of equimolar of Fe compound.

As shown in Table I, Samples 3e, 5e, 6e, 7e, 8e and 9e, the samples containing the combination of the pair metals exhibited unexpected superiority in comparison to Samples 3d, 5d, 6d, 7d, 8d and 9d, the samples containing a single metal.

## Conclusions

The present invention showed unexpectedly greater improvements of the samples containing the combination of the pair metals in sensitivity, printout performance and fogging during storage than the comparative examples.

# Experiment II

Samples 3a, 3b, 5a, 5b, 18a, 18b, 20a, 20b, 33a, 33b, 35a and 35b were prepared and added to the Additional comparative experiments in the declaration dated on September 13, 2005.

Samples 3a, 3b, 5a, 5b, 18a, 18b, 20a, 20b, 33a, 33b, 35a and 35b were prepared in the same manner as Samples in the declaration dated on September 13, 2005, except that the sum of the amount of the mercapto compound and the amount of the polyhalogen compound in the samples is equal.

Samples 3a, 3b, 5a, 5b, 18a, 18b, 20a, 20b, 33a, 33b, 35a and 35b were processed and evaluated sensitivity, fogging and printout performance in the same manner as in Example described in Applicants' Specification.

The results obtained are listed in following currently amended Table II.

TABLE II

Samole	ei) wor	1, 1								
No.		halide compositi on	mercapto hetero- ring compd.	mercapto hetero- ring compd. Amount mol/molAg	hetero- ring poly- halogen compd,		sensit ivity	fogging	Printout performance ADmin	Remarks
1 <b>–</b> 1	No. 1	AgBr	ı	1	r	mol/molAg	100	0.21	0.21	Comparative
										Example
2	No. 1	AgBr	. I-2	7.6×10-4	ı	1	142	0.16	0.18	Comparative
										Example
T)	No. 1	AgBr	1	1	No. 1	1.1×10 ⁻³	06	0.16	0.20	Comparative
										Example
Sa	No. 1	AgBr	1	1	No. 1	7.6×10 ⁻⁴	95	0.16	0.20	Comparative
č							1			Example
or or	No. 1	AgBr	I-2	3.8×104	No. 1	3.8×10-4	125	0.15	0.15	Comparative

Example Comparative	Example Comparative	Example Comparative	Example Comparative	Example Comparative	Example Comparative	Example Comparative Example
0.14	0.15	0.16	0.15	0.16	0.15	0.13
0,15	0.16	0.16	0.15	0.15	0.16	0.15
120	68	93	129	125	88	128
1.1×10 ⁻³	1.1×10 ⁻³	7.6×10-4	3.8×10-4	1.1×10 ⁻³	1.1×10-3	1,1×10 ⁻³
No. 1	No. 2	No. 2	No, 2	No. 2	No. 5	No. 5
7.6×10 ⁻⁴	1	I	3.8×10~	7.6x10-4	1	7.6×10 ⁻⁴
1-2			<b>I-</b> 2	[-2	ı	1-2
AgBr						
No. 1						
4	5	5a	56	ی	7	œ

თ	No. 1	AgBr	1	J	No. 6	1.1×10-3	106	0.16	0.14	Comparative
										Example
10	No.	AgBr	1-2	7.6×10 ⁻⁴	No. 6	1.1×10 ⁻³	94	0.15	0.13	Comparative
										Example
11	No. 1	AgBr	<u>1</u> .5	7.6×10 ⁻⁴	1	<u> 1 .</u>	138	0.17	0.16	Comparative
										Example
12	No. 1	AgBr	I-5	7.6×10 ⁻⁴	No.	1.1×10 ⁻³	106	0.15	0.15	Comparative
(										Example
£.1	No. 1	AgBr	5	7.6×10 ⁻⁴	No. 2	1.1×10 ⁻³	105	0.15	0.15	Comparative
										Example
57	No. 1	AgBr	I-5	7.6×10-4	No. 5	1.1×10 ⁻³	104	0.15	0.15	Comparative
L.										Example
13	No. 1	AgBr	I-5	7.6×10-4	No. 6	1.1×10 ⁻³	103	0.15	0.15	Comparative
										Examole
0 7	No. la	AgBr90110	ı	,		1	98	0.20	0.16	Comparative

11	No. 1a	AgBr90110	1-2	7.6×10-4	ı	ı	140	0.16	0.15	Example Comparative
										Example
18	No. 1a	AgBr90I10	1	1	No. 1	1.1×10 ⁻³	8.5	0.16	0.14	Comparative
										Example
18a	No. 1a	AgBr90110	ı	t	No. 1	7.6×10 ⁻⁴	95	0.16	0.15	Comparative
										Example
18b	No. 1a	AgBr90110	<b>I</b> ~2	3.8×10 ⁻⁴	No. 1	3.8×10 ⁻⁴	140	0.14	0.08	Present
										Invention
19	No. 1a	AgBr90110	[-2	7.6×10 ⁻⁴	No. 1	1.1×10 ⁻³	137	0.14	0.08	Present
										Invention
20	No. la	AgBr90110	1	I	No. 2	1.1×10 ⁻³	84	0.13	0.14	Comparative
										Example
20a	No. 1a	AgBr90110	,	1	No. 2	7.6×10-4	. 16	0.14	0.15	Comparative
										Example

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	4		$\overline{}$								
205	No. 1	1a	AgBr90110	1-2	3.8×10 ⁻⁴	No. 2	3.8×10-4	140	0.14	0.07	Present
											Invention
21	No. 1	1a	AgBr90110	[-2	7.6×10-4	No. 2	1.1×10 ⁻³	138	0.14	0.07	Present
											Invention
22	No. 1	1a	Ag8r90110	ı	1	No. 5	1.1×10 ⁻³	83	0.13	0.13	Comparative
											Example
23	No. 1	la	AgBr90110	[-2	7.6×10 ⁻⁴	No. 5	1.1×10 ⁻³	136	0.14	0.08	Present
											Invention
24	No. 1a	la a	AgBr90110	1	ı	Ко. 6	1.1×10 ⁻³	8.5	0.13	0.13	Comparative
											Бхащр1е
25	No. 1a	la	AgBr90110	I-2	7.6×10 ⁻⁴	No. 6	1.1×10 ⁻³	136	0.15	0.07	Present
											Invention
26	No. 1	la i	AgBr90110	I-5	7.6×10 ⁻⁴	r	ı	138	0.13	0,13	Comparative
											Example
27	No.	1a	AgBr90110	1-5	7.6×10-4	No. 1	1.1×10 ⁻³	135	0.14	0.08	Present

Invention	Present	Invention	Present	Invention	Present	Invention	Comparative	Example	Comparative	Example	Comparative	Example	Comparative	Example
<u>_</u>	4. E	r.	P.	ŗ.	Pr	In	Ö	Σ̈́	S	Ex	Con	č	Con	Exa
	0.08		0.08		0.08		0.12		0.11		0.11		0.12	
	0.14		0.14		0.14		0.17		0.15		0.13		0.14	
	139		140		137		95		141		82		5e	
	1.1×10 ⁻³		1.1×10 ⁻³		1.1×10 ⁻³		ı		1		1.1x10 ⁻³		7.6×10~	
	No. 2		No. 5		No. 6		ı		1		No. 1		No. 1	
	7.6×10-4		7.6×10 ⁻⁴		7.6×10~		1		7.6×10-4		1		ı	
	I-5		I-5		I-5		ı		<b>I-</b> 2		ı		t	
	AgBr90110		AgBr 90110		AgBr90110		AgBr10190		AgBr10190		AgBr10190		AgBr10190	
	Mo. 1a	,	NO. 18		No. 1a		No. 1b		No. 1b		No. 1b		No. 1b	
	28	29	3		30		31		32		££		33a	

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	No. 1 3.8×10 ⁻⁴ 144 0.14 0.06 Present	Invention	No. 1 1.1x10 ⁻³ 141 0.14 0.06 Present	Invention	No. 2 1.1x10 ⁻³ 84 0.13 0.11 Comparative	Example	No. 2 7.6x10 ⁻⁴ 97 0.14 0.12 Comparative	Example	No. 2 3.8×10 ⁻⁴ 143 0.14 0.06 Present	Invention	No. 2 1.1×10 ⁻³ 140 0.14 0.06 Present	Invention	No. 5 1.1x10 ⁻³ 83 0.13 0.11 Comparative	Example	NO 5
-	3.8×10 ⁻⁴ N		7.6×10 ⁻⁴ No		Ĭ		Z I		3.8×10-		7.6×10-4 No		NO NO		7.6x10-4 No
	190 1-2		90 1-2		- 06		- 06		90   I-2		90 1-2		<u> </u>		90 [-2
	o AgBr10190		AgBr10190		AgBr10190		AgBr10190		AgBr10190		AgBr10190		AgBr10190	<b>†</b>	AgBr10190
	33b No. 1b		34 No. 1b		35 No. 1b		JSa No. 1b	-	35b No. 1b		so No. 1b		No. Ib		33 NO. 1b

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ſ		(a)				a a			_	7		1			
	Invention	Comparative	Sxample	Present	Invention	Comparative	Example	Present	Invention	Present	Invention	Present	Invention	Present	Invention
		0.11		0.07		0.11		90.0		0.05		90.0		0.07	
		0.13		0.15		0.13		0.14		0.14		0.14		0.14	
		85		138		140		141		142		143		142	
		1.1×10 ⁻³		1.1×10 ⁻³		1		1.1×10 ⁻³		1.1×10 ⁻³		1.1×10 ⁻³		1.1×10 ⁻³	
		No. 6		No. 6		ı		No. 1		No. 2		No. 5		No. 6	
		1		7.6×10-4		7.6×10 ⁻⁴		7.6×10 ⁻⁴		7.6×10 ⁻⁴		7.6×10-4		7.6×10-4	
		1		1-2		1-5		I-5		1-5		5-		I-5	
		AgBr10190		AgBr10190		AgBr10190		AgBr10190		AgBr10 <u>5</u> 90		AgBr10190		AgBr10190	
		No. 1b		No. 1b		No. 1b		No. 1b		No. 15		No. 1'b		No. 15	
		39		40		쇼 네 ·		75		£5		<i>†</i> †		C F	

Sensitivity is shown as a relative value taking the sensitivity of Sample No. 1 to be 100.

As seen in Table II above, the combination of the silver halide emulsion, the mercapto hetero-ring compound and the hetero-ring polyhalogen compound of the present invention were unexpectedly superior in fogging and printout performance ( $\Delta Dmin$ ) in comparison to the comparative examples, while maintaining high sensitivity.

In the combinations of mercapto hetero-ring compound and hetero-ring polyhalogen compound in the examples of the present invention,  $\Delta D$ min decreases by 0.06-0.08, and  $\Delta D$ min is lower than 0.1.

### Conclusions

The present invention showed unexpectedly greater improvements of the the samples containing the combination of the mercapto hetero-ring compound and hetero-ring polyhalogen compound in sensitivity, printout performance and fogging during storage than the comparative examples.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

DATE: April 7, 2006

Seiichi Yamamoto